

Picosecond Kinetics and Reverse Saturable Absorption of Meso-Substituted Tetrabenzoporphyrins

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The mechanism of reverse saturable absorption of meso-substituted tetrabenzoporphyrins was studied by means of picosecond transient spectroscopy. Characteristic $^1(\pi,\pi^*)$, $^3(\pi,\pi^*)$, and (d,d) transitions have been observed. The kinetics of the excited states vary with metal substitution. The nonlinear transmission of benzoporphyrins was measured, and the excited-state absorption was determined to be the dominant optical limiting mechanism. The results agreed very well with a five-level model.

I. Introduction

Studies on the optical nonlinear properties of the organic molecules with π electron delocalization have drawn considerable attention for a long period of time¹ because of their large and fast nonlinear optical response and capability to be easily engineered for a particular purpose. Among these molecules, porphyrins are one of the most studied class of compounds because of their importance and abundance in nature. Because of their large π -conjugated systems, several derivatives have been synthesized to exhibit large nonlinear optical properties.²

The rapid advancements in high-power laser technology have increased the necessity to protect sensors and human eyes from high-energy laser damage. It becomes therefore an important issue to search for materials to be used as the optical limiting devices. The basic concept of optical limiting introduced by Leite et al.,³ relied on the properties of the optical nonlinear materials which are transparent under normal condition but become opaque when exposed to high fluence of optical radiation. Recent studies showed that several compounds which exhibited reverse saturable absorption demonstrated promising optical limiting power.⁴⁻⁸ In contrast to saturable absorption, the absorption of reverse saturable absorption materials increases as the incident intensity increases. This phenomenon can be understood in terms of excited-state absorption. If the absorption cross section of the excited state, σ_{ex} , is much larger than the cross section of the ground state, σ_{gr} , then at low incident intensities, the material is transparent because of the low absorption coefficient for the ground state and the low occupation in the excited state. As the intensity increases, the population of the excited state will increase and the effective absorption coefficient will also increase if the lifetime of the excited molecules is longer than the incident pulse duration. In the saturation limit, the ground state will be practically depleted, and the effective absorption coefficient of the materials will be governed by the absorption among excited states, because of their larger absorption cross section. These types of materials can be used as the optical limiters. The basic requirements for optical limiting materials⁹ are the following: (1) $\sigma_{gr} \ll \sigma_{ex}$, so the molecules in their excited state are more likely to absorb light than in the ground state. (2) The lifetime of the excited state should be longer than the incident laser pulse duration in

order to accumulate the population in the excited state. However, it should become transparent shortly after the incident laser pulse. (3) The materials should have a high optical damage threshold. (4) To be effective against a range of wavelengths, the optical limiting materials should exhibit a broadband transient absorption which covers the entire visible region. (5) The response time should be fast enough to limit the destructive effect from the incident laser. Since the mechanism of optical limiting depends on the absorption of the excited molecules, it is important to study and identify the spectra and kinetics of the intermediate states of optical limiting materials, to maximize the use of materials as optical limiting devices.

Some porphyrin and phthalocyanine derivatives have been reported to exhibit reverse saturable absorption properties;^{7,10} however, the optical limiting powers among these derivatives were quite different. Therefore, it is important to know the substitution effects on optical limiting through the kinetic and spectroscopic studies. For this reason, we have investigated six metallo *meso*-tetraaryltetrabenzoporphyrins (heretofore we shall refer to these as the benzoporphyrins). The nonlinear optical properties of some meso-substituted benzoporphyrins have been reported lately, and the excited-state absorption was found to be the dominant factor for their nonlinear properties.¹¹ It is our goal to understand the relationship between the excited-state kinetics and the optical nonlinear properties in benzoporphyrins. We first studied their transient spectra and kinetics and then compared our data with existing information on similar porphyrins.¹²⁻¹⁵ We were able to identify several characteristic kinetic and spectroscopic features for these benzoporphyrins. After measuring the absorption cross section for both ground and excited states of these six benzoporphyrins, we used a five-level rate equation to calculate the energy-dependent transmission. The calculated values agreed with our experimental data quite well.

In general, porphyrins with D_{4h} symmetry (planar configuration) exhibit two main transitions in the UV-visible region, a weak visible Q-band and a strong near-UV, B (Soret)-band.¹⁶ Different substitutions change the position of these bands, but the separation between the Q-band and B-band remains roughly the same. The tetrabenzoporphyrins showed red-shifted spectra compared with porphyrins because of more delocalized π electrons on the macrocycle. Table 1 shows the B-band and Q-band absorption maxima and the molar absorption coefficients for all the benzoporphyrins we investigated. The molar absorption coefficients of excited states were measured at 40 ps time

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TABLE 1: Absorption Coefficients ($\text{mM}^{-1} \text{cm}^{-1}$)

substance	B-band		Q-band		excited state ^a	
	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
ZnTPTBP	462	224	652	47	510	19
CuTMPTBP	467	131	647	43	550	11
NiTPTBP	448	220	643	88	480	10
NiTMPTBP	453	200	643	71	480	9
PtTPTBP	429	76	613	47	470	11
PtTMPTBP	435	43	613	25	460	8

^a The detail assignment in the text.

delay intervals. The absorption origins were different for different benzoporphyrins, and detail assignments will be presented in the discussion section.

To optimize the optical limiting power, it is desirable to increase the cross-section ratio, $\sigma_{\text{ex}}/\sigma_{\text{gr}}$. The wavelength of the excitation pulse, the second harmonic of the YAG laser, lies in the minimum absorption region between B-band and Q-band absorption maxima. This effectively increases the cross-section ratio, if the excited-state absorption cross section remains the same. However, due to the low absorption at this excitation wavelength, the concentrations of the benzoporphyrins were relative high ($>10^{-4} \text{ M}$).

We investigated the transient spectra and kinetics of six different benzoporphyrin derivatives by means of picosecond transient spectroscopy. This technique has been well established for the study of transient species.¹² The advantages of this technique are the following: First, the time resolution is the same as the laser pulse duration which can be as short as tens of femtoseconds. Second, unlike fluorescence measurements, this technique can be applied to probe radiationless transitions and absorption spectra. Third, with a CCD detector, both spectra and kinetic information can be obtained simultaneously. Our data showed that the energy relaxation process of the meso-substituted benzoporphyrins studied were quite different. For Zn and Pt benzoporphyrins, the transient absorption lasted as long as nanoseconds, but for Ni and Cu benzoporphyrins, the transient absorption disappeared within 100 ps.

II. Experimental Section

General methods of synthesis of Zn meso-tetraaryl-tetrabenzoporphyrins have been described by Remy et al.¹⁸ The free benzoporphyrin bases were obtained by treating the zinc derivatives with trifluoroacetic acid. The free base was treated in dimethylformamide with either Cu(II) acetate, Ni(II) acetate, or Pt(II) chloride. The mixture was refluxed overnight, and the solvent was removed at water aspirator pressure to dryness. The residue was treated with methylene chloride/1% pyridine. The solution was washed with water, and the solvent was removed as above. The purification of the metallobenzoporphyrins was done by a small-scale silica column or preparative thin-layer chromatography. The eluent was the methylene chloride-pyridine mixture.

The laser system used in these measurements was a passive mode-locked Nd:YAG oscillator with 35 ps pulse duration. A single pulse was selected by a Pockels cell which was split into two parts and amplified by two double-pass amplifiers. The output from the first amplifier was focused by a 15 cm focal lens into a 15 cm cell filled with a mixture of H_2O and D_2O , to generate a picosecond continuum, followed by another lens to recollimate the continuum beam. An ND 1 filter and a Corning 4-69 filter were used to select a continuum in the range 400–800 nm. The continuum was then split by a 50% beam splitter to two parts; one part was used to probe the solution containing the sample, and the other passed through the reference cell

containing pure solvent. The signal and the reference beams were focused onto the slit of a spectrograph with 6 mm separation distance. A liquid nitrogen cooled 256×1024 pixel CCD detector (Princeton Instruments) was mounted on the output of a spectrograph. Two sections of the CCD with 20×1 binning (1 pixel binning along wavelength axis) were used to record the sample and reference signals. When the second harmonic radiation was used for excitation, a Raman notch filter was placed in front of the spectrograph to block the second-harmonic scattered light.

The output from the second amplifier was used to generate the $\sim 3 \text{ mJ}$ second harmonic in a KDP crystal. A KG3 filter was used to filter out the fundamental radiation. The excitation beam was then focused by a 1 m lens to a 2.5 mm diameter spot. For kinetic measurements, all the benzoporphyrin samples were dissolved in benzene at a concentration equivalent to an absorbance of 0.5–1 at 532 nm in a 1 cm optical path cell. The excitation energy was monitored by means of a Moletron J-4 energy meter. The kinetic measurements were performed at the region where there was no saturation effect, namely at low excitation energy. For each data point, two consecutive measurements were made, one with and the other without excitation. Together with the reference spectrum, four spectra were used to calculate the transient absorbance. This procedure minimized the possible energy fluctuation in the continuum. Normally 80 shots, per spectrum, were averaged and used to calculate the absorbance, and the transient spectra were further smoothed by five-point averaging.

Nonlinear transmission measurements were carried out with an unfocused 3 mm diameter second-harmonic beam. The benzoporphyrins were dissolved in benzene to a concentration equivalent to 30% transmission at 532 nm in a 1 cm optical path cell. A set of ND filters was used to vary the incident energy from 0.05 to 2 mJ.

III. Results and Discussion

In this study, we investigated six benzoporphyrins: zinc meso-tetraphenyltetrabenzoporphyrin (ZnTPTBP), copper meso-tetrakis(p-methoxyphenyl)tetrabenzoporphyrin (CuTMPTBP), nickel meso-tetraphenyltetrabenzoporphyrin (NiTPTBP), nickel meso-tetrakis(p-methoxyphenyl)tetrabenzoporphyrin (NiTMPTBP), platinum meso-tetraphenyltetrabenzoporphyrin (PtTPTBP), and platinum meso-tetrakis(p-methoxyphenyl)tetrabenzoporphyrin (PtTMPTBP). The kinetic behavior varies quite considerably for different porphyrins. We will discuss the kinetics and mechanism of these benzoporphyrins and then use the rate equations to calculate the picosecond nonlinear transmission and compared these results with our experimental data.

A. Mechanism. (a) *ZnTPTBP*. Previous transient measurements¹² of Zn porphyrin derivatives showed that the lifetime of the excited singlet states were about 2.5 ns. These transient spectra have characteristic $^1(\pi, \pi^*)$ and $^3(\pi, \pi^*)$ absorptions which exhibit very strong absorption between the ground-state B-band and the Q-band bleachings. Rodriguez et al.^{12b} pointed out that the transient spectra in this region were not distinguishable because of band overlapping. However, the $^1(\pi, \pi^*)$ level exhibits a unique Q(0,1) stimulated emission which should be at the same position as the spontaneous Q(0,1) emission, and the $^3(\pi, \pi^*)$ transition can be marked by the distinct near-infrared absorption peak. Figure 1 shows the transient spectra of ZnTPTBP at various time delays. A strong transient absorption at 500 nm was observed. The dip in the absorption band around 532 nm was due to the Raman notch filter used to eliminate the scattered second-harmonic light. After a fast rise, the intensity of the transient absorption maximum remained at the

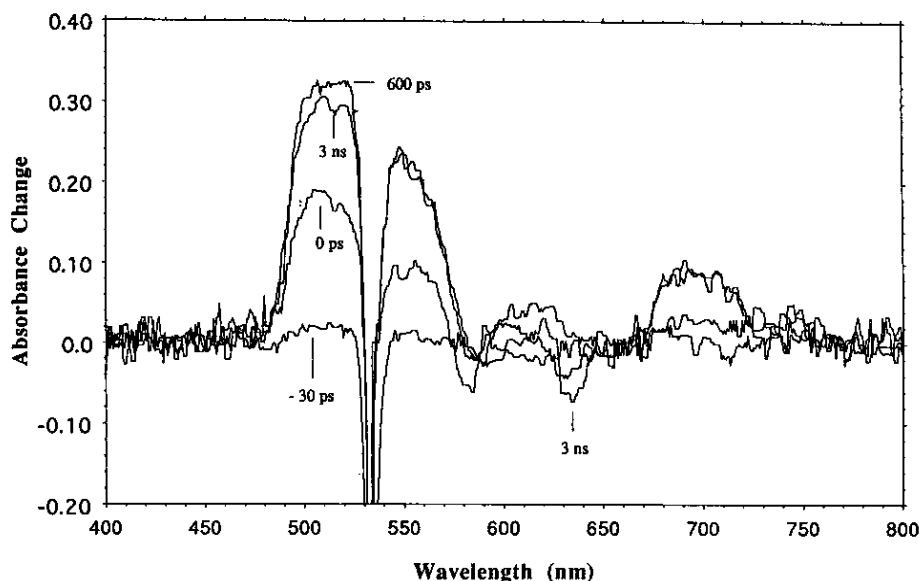


Figure 1. Transient spectra of ZnTPTBP in benzene at various time delays.

same absorbance for about 5 ns, but shifted slightly to the red at longer time delay. This behavior is the same as the one observed in the zinc tetraphenylporphyrin (ZnTPP). The transient absorption maximum and absorption coefficients of the excited singlet states and triplet states were very close to those found in ZnTPTBP. It was practically impossible to extract any useful information in the 500 nm region. To evaluate the relaxation time of the excited states, we have looked for their characteristic behaviors, the Q(0,1) stimulated emission and the near-infrared absorption. We did not observe any stimulated emission in our experiments, probably because of the low emission intensity of the Q(0,1) benzoporphyrins band and of the low continuum intensity at the wavelengths longer than 720 nm owing to the Raman notch filter. However, we did observe the transient absorption of the excited singlet state around 600 nm and determined the lifetime of the excited singlet state to be 650 ps. We also observed a slowly rising component around 700 nm which is the characteristic absorption of the triplet state. From the data of ZnTPTBP in benzene, we know that the lowest excited singlet state exhibits a broad band absorption which extends to 600 nm and a lifetime of less than 1 ns. The lowest excited triplet state also has its absorption maximum in the 500 nm region; however, it has a characteristic absorption in the 700 nm region that reaches its maximum absorption intensity after 1 ns.

(b) *CuTMPTBP*. Cu(II) has an unpaired d-electron which interacts with the porphyrin π electrons. As a result of this coupling the energy levels of this porphyrin are modified.¹⁹ Under these conditions, the ground state becomes a singdoublet 2S_0 and the lowest excited singlet state becomes singdoublet 2S_1 . Alternatively, the triplet states $^3(\pi, \pi^*)$ split into a tripdoublet $^2T(\pi, \pi^*)$ and quartet $^4T(\pi, \pi^*)$. Because of the admixing between the excited singdoublets into the tripdoublets by exchange interactions, an additional transition was observed for CuTMPTBP around 920 nm. Kobayashi et al.^{13a} reported that the relaxation process for copper protoporphyrin IX dimethyl ester (CuPPDME) was from the lowest excited singdoublet state 2S_1 to the lowest tripdoublet $^2T(\pi, \pi^*)$ within 8 ps and then to a thermal equilibrium state between $^2T(\pi, \pi^*)$ and $^4T(\pi, \pi^*)$ with a time constant of 450–460 ps. Using phosphorescence measurements at room temperature, the lifetime of the $^2T(\pi, \pi^*)$ component of the thermal equilibrium state was estimated to be longer than 1 ns.²⁰ However, kinetic measurements of copper tetraphenylporphyrin (CuTPP) and Cu(Etio) in toluene showed

that the transient absorption and bleaching were dominated by two components, a major component which lasted for more than 10 ns and a smaller absorption component which relaxed in less than 500 ps.^{13b} The relaxation of the excited singdoublet state 2S_1 , was believed to relax to tripdoublet $^2T(\pi, \pi^*)$ within the excitation pulse duration and the major component was assigned to the transient absorption of the 2T and/or 4T state. In our studies of CuTMPTBP, only one major relaxation rate was determined. There may be a weak component which lasts more than 1 ns. However, the amplitude of this weak component was too small for accurate kinetic evaluation. Figure 2 shows the transient absorption spectra of CuTMPTBP, after excitation with a 532 nm pulse.²¹ The kinetics of this band are composed of an instrument-limited rise time and a relative fast decay (~ 50 ps) (Figure 3). The transient absorption spectrum of CuTMPTBP is very similar to that of ZnTPTBP, except that the absorption maximum is shifted to the red. At zero time delay, the spectrum exhibited an absorption peak around 550 nm and a weak red tail extended to 650 nm. The red tail was only observed at zero time delay and may be attributed the absorption of the 2S_1 state which relaxed to the tripdoublet 2T_1 state within the pulse duration. Kim et al.^{13b} indicated that the absorptions of 2T_1 and 4T_1 states were roughly the same, and 50 ps relaxation time of the 550 nm absorption band may be attributed to the relaxation of thermal equilibrium state of 2T_1 and 4T_1 .

Compared with the relaxation time of other Cu porphyrin derivatives in noncoordinated solvents, 50 ps is too fast for the relaxation of the equilibrium state. A reasonable explanation is the formation of dimers or aggregates^{13d,22} which contain more charge-transfer character than monomer and lead to a fast intersystem crossing process. In this study we did not identify the existence of the dimers.

(c) *NiTPTBP and NiTMPTBP*. The electronic configuration of Ni(II) is d^8 and the lowest three d-orbitals, d_{xy} , d_{yz} , and d_{xz} , are always filled up with electrons when incorporated into porphyrins. Depending on the number of coordination, the last two electrons can either fill up the d_z^2 or occupy both the d_z^2 and the $d_{x^2-y^2}$ orbitals. Ake and Gouterman²³ showed that in four-coordination Ni porphyrins, the electron configuration of the ground state is $(d_z^2)^2$. Previous measurements showed that there were two relaxation processes for the transient of nickel protoporphyrin dimethyl ester (NiPPDME),^{12a} one with 10 ps and the other with 250 ps lifetime. Because there are many

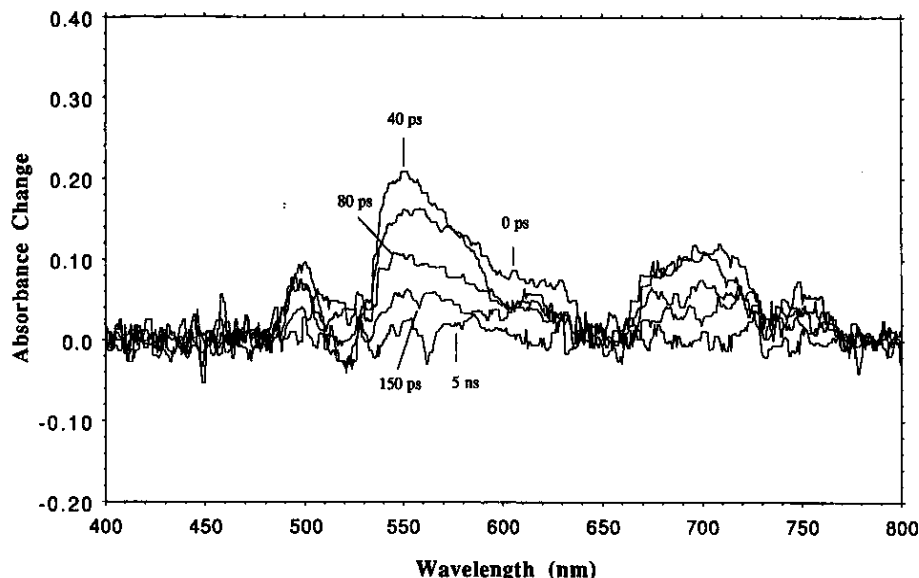


Figure 2. Transient spectra of CuTMPTBP in benzene at various time delays.

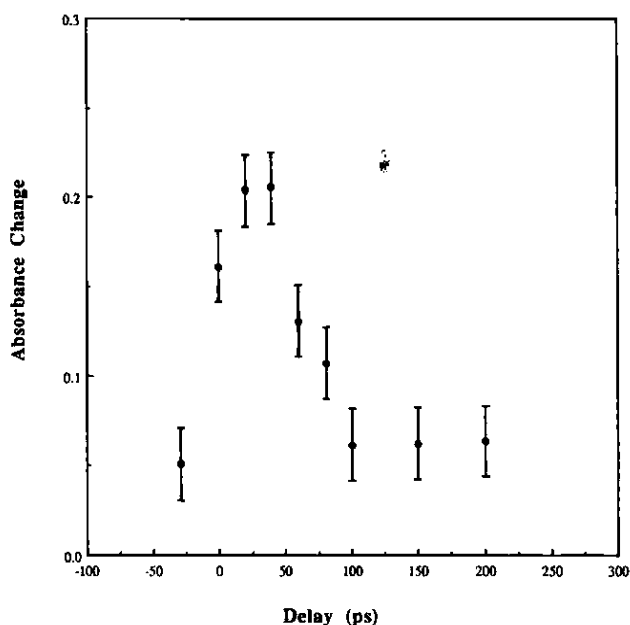


Figure 3. Kinetics of CuTMPTBP at 550 nm.

possible relaxation pathways through the low-lying metal state, different investigations have led to different conclusions.^{12a,14} Recent studies of Ni porphyrins concluded that, for NiTPP in noncoordinated solvents,²⁴ the energy was transferred from the initial excited $^1Q(\pi, \pi^*)$ state which is localized on the macrocycle to the low-lying metal (d_z^2 , $d_{x^2-y^2}$) state within 350 fs. And the macrocycle returned to its ground-state configuration in the same period of time. However, the excess energy increased the internal vibrational energy which was responsible for the change in transient absorption for the first 20 ps. The lifetime of the low-lying metal state was about 250 ps. They also pointed out that the (d,d) excited states exhibited two characteristic spectral features: a sharply featured spectrum near 350–600 nm and the absence of absorption in the red. When the Ni tetrabenzoporphyrin derivatives were dissolved in benzene, the transient spectra showed a strong absorption at 480 nm. Figure 4 shows the transient absorption spectra of NiTPTBP in benzene. The transient spectrum exhibited a relatively sharp absorption maximum compared with other tetrabenzoporphyrin derivatives except at zero time delay, where the spectrum extended to the red. In NiTPP and NiPPDME,

these red tail absorptions were also observed, and therefore, they may be associated with the unrelaxed vibrational components. In general, the transient absorption of nickel tetrabenzoporphyrin derivative possessed the characteristic (d,d) absorption, a sharp absorption maximum between Soret and Q-band, and an absorption at the red of the ground-state bleaching (around 650 nm).²⁵ Therefore, the relaxation process for both Ni porphyrins are through the low-lying metal state. The lifetime of this low-lying metal state is about 45 ps for NiTPTBP and 65 ps for NiTMPTBP.

(d) *PtTPTBP and PtTMPTBP.* As the atomic number of the metal core of porphyrins increases, we expect that the intersystem-crossing rate will also increase. It is known that Pt porphyrins do not fluoresce but phosphoresce. All the measurements of Pt porphyrins¹⁵ showed that the lifetimes of the excited singlet states were less than 10 ps, and the transient absorptions in the pico–nanosecond time scale are mainly due to $^3(\pi, \pi^*)$ absorption. In our study, both PtTPTBP and PtTMPTBP transient spectra showed characteristic $^3(\pi, \pi^*)$ absorption, a broad absorption maximum between Soret and Q-band, and a weak absorption at the red of Q-band absorption. The intensity of the transient absorption maximum remained the same up to 5 ns. Therefore, we conclude that the lifetimes of the excited singlet state for both PtTPTBP and PtTMPTBP are less than the pulse duration and the transient absorption we observed belongs to the triplet–triplet transition.

B. Picosecond Nonlinear Transmission. The optical limiting effect of the reversed saturable absorption materials relies on the absorption of the excited state. At low incident radiation, the absorption process is mainly due to the ground state; therefore, the transmittance is

$$T = \frac{I_T}{I_0} \exp[-\sigma_g \int_0^L N_0(z) dz]$$

where I_T and I_0 are transmitted and incident intensities, σ_g is the absorption cross section of the ground-state molecule, and N_0 is the concentration. However, at the saturation limit, the absorption is dominated by the excited molecules, and therefore, the transmitted light intensity may be expressed as

$$I_s = I_0 \exp[-\sigma_e \int_0^L N_0(z) dz]$$

If we define the signal suppression,²⁶ S , as

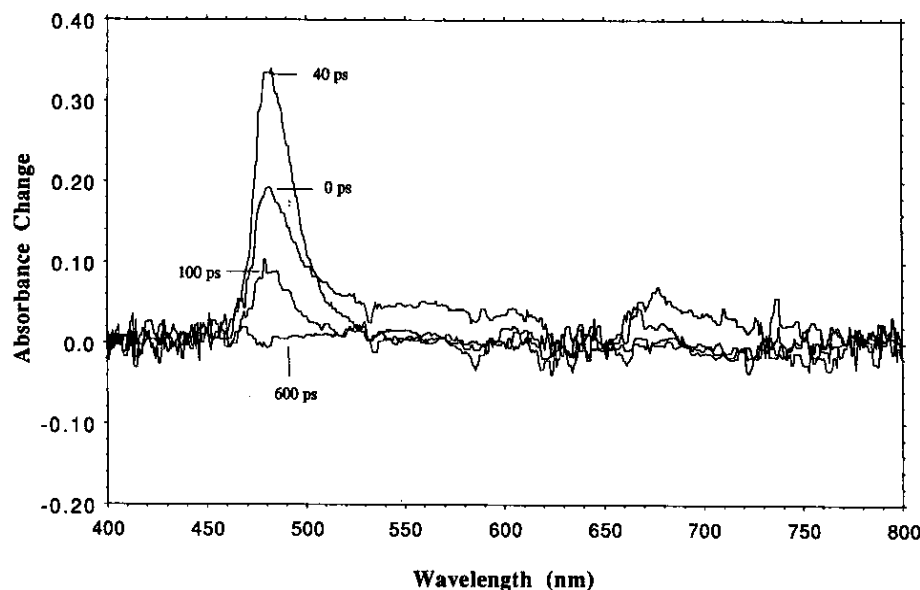


Figure 4. Transient spectra of NiTPTBP in benzene from 0 to 600 ps.

$$S = \frac{I_0}{I_s} = \exp[\sigma_e \int_0^L N_0(z) dz]$$

then

$$\frac{\ln S}{-\ln T} = \frac{\sigma_e}{\sigma_g}$$

Table 2 shows the absorption cross section of the ground and excited states (measured at 40 ps time delay) for tetrabenzoporphyrin derivatives at 532 nm. ZnTPTBP exhibits the largest cross section ratio. Figure 5 shows the nonlinear transmission of ZnTPTBP/benzene solution under a different picosecond 532 nm pulse energy. The concentration of the solution was about 100 μ M, and the linear transmission about 30%; in this case, the suppression is 142. As the incident energy increased, the transmission decreased to 15%. To calculate the energy-dependent transmission, we used a set of rate equations based on a five-level system. These rate equations are^{8,27}

$$\frac{dS_0}{dt} = -\sigma_{01}S_0\Phi + K_{10}S_1 + K_{30}T_1 \quad (1)$$

$$\frac{dS_1}{dt} = \sigma_{01}S_0\Phi - \sigma_{12}S_1\Phi - K_{10}S_1 - K_{13}S_1 + K_{21}S_N \quad (2)$$

$$\frac{dS_N}{dt} = \sigma_{12}S_1\Phi - K_{21}S_N \quad (3)$$

$$\frac{dT_1}{dt} = -\sigma_{34}T_1\Phi - K_{30}T_1 + K_{13}S_1 + K_{43}T_N \quad (4)$$

$$\frac{dT_N}{dt} = \sigma_{34}T_1\Phi - K_{43}T_N \quad (5)$$

and the propagation equation is

$$\frac{d\Phi}{dz} = -\sigma_{01}S_0\Phi - \sigma_{12}S_1\Phi - \sigma_{34}T_1\Phi \quad (6)$$

where $S_{0,1,N}$ and $T_{1,N}$ are the concentrations of the different levels (Figure 6), Φ is the photon flux, σ is the absorption cross section, and K is the relaxation rate constant between each state. The relaxations from excited manifolds are believed to take place

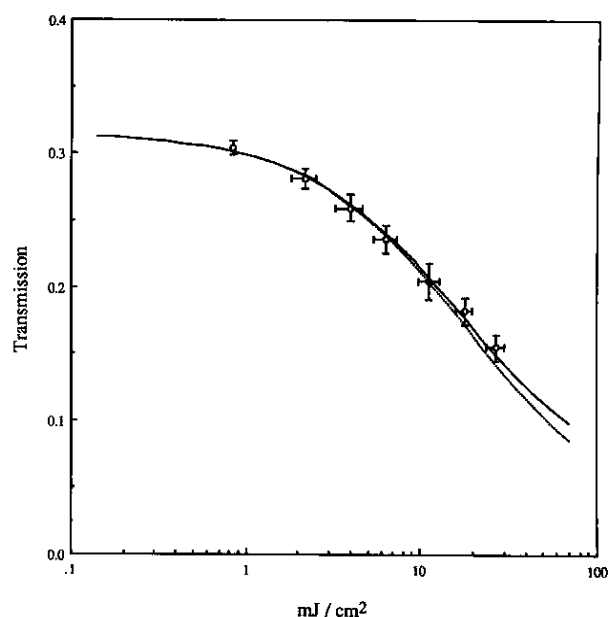


Figure 5. Nonlinear transmission of ZnTPTBP. The linear transmission is 30%. The circles are experimental data, the solid line is calculated using the five-level model. The dashed line is calculated using steady-state assumption.

TABLE 2: Absorption Cross Sections (10^{-17} cm²) at 532 nm

substance	σ_{01}	σ_{12}
ZnTPTBP	1.7	7.2
CuTMPTBP	3.0	4.3
NiTPTBP	1.5	1.6
NiTMPTBP	2.0	2.3
PtTPTBP	1.7	3.4
PtTMPTBP	1.3	2.1

within 1 ps; therefore, K_{21} and K_{43} were taken to be $(1 \text{ ps})^{-1}$. K_{10} , K_{30} , and K_{13} are all smaller than 10^9 and have little effect on the calculations. The cross sections of the excited states were measured by means of picosecond transient spectroscopy. By making the steady-state assumption of the highly excited manifolds, we were able to reduce the rate equations¹⁰ to

$$\frac{dS_0}{dt} = -\sigma_{01}S_0\Phi + K_{10}S_1 + K_{30}T_1 \quad (7)$$

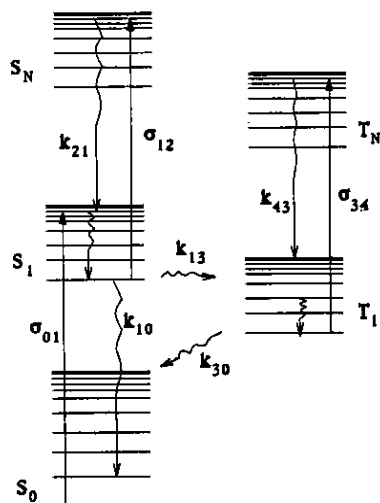


Figure 6. Five-level kinetic model for ZnTPTBP.

$$\frac{dS_1}{dt} = \sigma_{01}S_0\Phi - K_{10}S_1 - K_{13}S_1 \quad (8)$$

$$\frac{dT_1}{dt} = -K_{30}T_{31} + K_{13}S_1 \quad (9)$$

Figure 5 shows both experimental data and calculated values using by two sets of rate equations. Both sets of rate equations agreed very well with the experimental data, and the differences in calculated transmission between these two sets of rate equations were small. For ZnTPTBP, the relaxation time from the $^1(\pi,\pi^*)$ state to the $^3(\pi,\pi^*)$ state was by far longer than the laser pulse duration; therefore, only the $^1(\pi,\pi^*)$ state was involved in the optical limiting mechanism. Our calculation showed that the population of the $^1(\pi,\pi^*)$ state increased significantly as the optical limiting effect became operative.

IV. Conclusion

We have observed several characteristic spectroscopic and kinetic features for various metal-substituted tetrabenzoporphyrins. ZnTPTBP exhibited both $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ transitions, while the heavy atom substituted PtTPTBP and PtTMPTBP showed only $^3(\pi,\pi^*)$ absorption. We also observed a (d,d) transition in NiTPTBP and NiTMPTBP. However, no large changes were observed between *meso-p*-methoxyphenyl and *meso*-phenyl derivatives. Some relaxation rates measured in our experiments were found to be much faster than those observed in other porphyrin derivatives.

A major concern of this study is the optical limiting power of the benzoporphyrins, which requires a large ratio of absorption cross section between ground and excited states and a rather longer lived excited state compared to the pulse duration. We found that the optical limiting effect of ZnTPTBP depended on the population of the first excited singlet state. The experimental data confirmed that the excited-state absorption was the dominant mechanism of the optical limiting in ZnTPTBP. The absorption cross sections of the excited states were dominated by the characteristic absorption of the $^1(\pi,\pi^*)$ or $^3(\pi,\pi^*)$ transition of the macrocycle. Because the ground-state absorptions were quite different for different substituents, it is possible

to select the proper substituent on the porphyrins and increase their absorption cross section ratio, which will also increase the optical limiting power. The fact that the absorption cross sections of the lowest excited singlet state and the lowest triplet state of ZnTPTBP were roughly the same suggests that this material is also a good optical limiting material for intense nanosecond pulses.

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